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# SCREENING TESTS OF ESTERS OF PIPERONYL ALCOHOLS AS INSECTICIDES

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In a previous report[1/] it was shown that the chrysanthemumic acid esters of a series of piperonyl alcohols exhibited considerable activity as louse toxicants, mosquito larvicides, and synergists. In a continuation of this work, we have prepared other esters of these piperonyl alcohols in which various organic acids have been substituted for chrysanthemumic acid.

The structure and physical properties of the esters are listed in table 1.

These compounds were tested at the Orlando, Fla., laboratory in routine fashion by the methods described by King[2/] The results of the tests against mosquito repellents and synergists for pyrethrins and allethrin are listed in table 2.

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1/ Chen, Y. L., and W. F. Barthel. 1956. Screening tests of esters of chrysanthemumic acid as synergists and insecticides. U. S. Agr. Res. Serv. ARS-33-23, 10 pp.

2/ King, W. V. 1954. Chemicals evaluated as insecticides and repellents at Orlando, Fla. U. S. Dept. Agr. Handbook 69, 397 pp. Carroll N. Smith, M. M. Cole, and J. C. Keller conducted the biological tests. Their entomological studies with compounds of special interest will be published elsewhere.

## Key to Biological Activity of Compounds Shown in Table 2

The classification given below is the same as that used in the King report except for the synergist data.

### Toxicants

Mosquito Larvae

1. Less than 50 percent mortality at 10 p.p.m.
2. 50 to 94 percent at 10 p.p.m.
3. 95 to 100 percent at 10 p.p.m. but less than 50 percent at 1 p.p.m.
4. 50 to 100 percent at 1 p.p.m.

4A. 95 to 100 percent at 0.01 p.p.m.

Body Lice

1. Ineffective.
2. Effective (no survivors) on the initial exposure but ineffective on the second exposure started 1 day after treatment.
3. Effective on the second exposure but failed on or before the 10th day.
4. Effective for 10 days or more.

4A. Effective for 31 days or more.

Chiggers

1. Ineffective on initial test.
2. Effective on control test but ineffective after a 15-minute rinse.
3. Effective after the rinse but not after three washings.
4. Effective after three or more washings.

4A. Effective after five washings.

### Synergists

Body Lice and House Flies

Inef. No decided synergist activity.
3. Some synergism but less than standard.
4. As effective as standard.

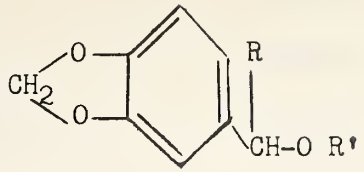
The standard synergist for body lice is sulfoxide, and for house flies piperonyl butoxide.

### Repellents

Mosquitoes (tests on cloth)

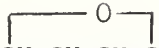
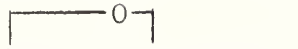
1. Ineffective on the initial test (5 or more bites in 1 minute).
2. Effective for 1 to 5 days.
3. Effective for 6 to 10 days.
4. Effective for more than 10 days.

Table 1.--Esters of piperonyl alcohols




| Item No. | R | R' | Empirical formula | Boiling point | | $N_D^{25}$ |
|---|---|---|---|---|---|---|
| | | | | °C. | mm./Hg | |
| 1 | H | HCO | $C_9H_8O_4$ | 87 | 0.05 | 1.5440 |
| 2 | H | $(CH_3)_2C=CHCO$ | $C_{13}H_{14}O_4$ | 191-200 | 20 | 1.5385 |
| 3 | H | $(CH_3)_3CCO$ | $C_{13}H_{16}O_4$ | 113-115 | .3 | 1.5028 |
| 4 | H | $C_6H_5CO$ | $C_{15}H_{12}O_4$ | - | - | mp 68-69° |
| 5 | H | $C_6H_5CH_2CH_2CO$ | $C_{17}H_{16}O_4$ | 231 | 8 | 1.5611 |
| 6 | H | $CH_2=CH(CH_2)_8CO$ | $C_{19}H_{26}O_4$ | 177-182 | .1 | 1.5037 |
| 7 | H | o-$C_2H_5OC_6H_4CO$ | $C_{17}H_{16}O_5$ | 201 | 1.2 | 1.5723 |
| 8 | H | $C_6H_5SO_2$ | $C_{14}H_{12}O_5S$ | - | - | mp 69-69.5° |
| 9 | $CH_3$ | $CH_3CO$ | $C_{11}H_{12}O_4$ | 114-120 | 1 | 1.5298 |
| 10 | $CH_3$ | $CH_2=CH(CH_2)_8CO$ | $C_{20}H_{28}O_4$ | 169 | .1 | 1.4977 |
| 11 | $CH_3$ | $C_6H_5CH_2CO$ | $C_{17}H_{16}O_4$ | 167 | .1 | 1.5598 |
| 12 | $C_2H_5$ | $CH_3CO$ | $C_{12}H_{14}O_4$ | 120-124 | 3 | 1.5152 |

Table 1.--Continued

| Item No. | R | R' | Empirical formula | Boiling point | | $N_D^{25}$ |
|---|---|---|---|---|---|---|
| | | | | °C. | mm./Hg | |
| 13 | $C_3H_7$ | $CH_3CO$ | $C_{13}H_{16}O_4$ | 134-136 | 3 | 1.5084 |
| 14 | $C_3H_7$ | $CH_3CH_2CO$ | $C_{14}H_{18}O_4$ | 141-145 | 3 | 1.5035 |
| 15 | $(CH_3)_2CH$ | HCO | $C_{12}H_{14}O_4$ | 158 | 10 | 1.5202 |
| 16 | $(CH_3)_2CH$ | $CH_3CO$ | $C_{13}H_{16}O_4$ | 130-135 | 3 | 1.5118 |
| 17 | $(CH_3)_2CH$ | $C_6H_5CH_2CO$ | $C_{19}H_{20}O_4$ | - | - | *1.5671 |
| 18 | $CH_2=CHCH_2$ | $CH_3CO$ | $C_{13}H_{14}O_4$ | 157-160 | 4 | 1.5259 |
| 19 | $CH_2=CHCH_2$ | $CH_3CH_2CO$ | $C_{14}H_{16}O_4$ | 186-188 | 18 | 1.5180 |
| 20 | $CH_2=CHCH_2$ | $(CH_3)_2C=CHCO$ | $C_{16}H_{18}O_4$ | 163-174 | 3 | 1.5338 |
| 21 | $CH_2=CHCH_2$ | $(CH_3)_3CCO$ | $C_{16}H_{20}O_4$ | 142-148 | 2 | 1.5100 |
| 22 | $CH_2=CHCH_2$ | $CH_3(CH_2)_4CO$ | $C_{17}H_{22}O_4$ | 156-159 | 2 | 1.5104 |
| 23 | $CH_2=CHCH_2$ | $CH_3(CH_2)_{14}CO$ | $C_{27}H_{42}O_4$ | - | - | *1.4915 |
| 24 | $CH_2=CHCH_2$ |  | $C_{16}H_{14}O_4$ | 184-187 | 2 | 1.5605 |
| 25 | $CH_2=CHCH_2$ |  | $C_{18}H_{16}O_5$ | 115-130 | 0.025 | semisolid |
| 26 | $CH_2=CHCH_2$ | $CH_2=CH(CH_2)_8CO$ | $C_{22}H_{30}O_4$ | 194-206 | .1 | 1.5025 |
| 27 | $CH_2=CHCH_2$ | $C_6H_5CO$ | $C_{18}H_{16}O_4$ | 200-210 | 18 | mp 40° |
| 28 | $CH_2=CHCH_2$ | $C_6H_5CH_2CO$ | $C_{19}H_{18}O_4$ | 202 | 3 | 1.5635 |

| | | | | | | |
|---|---|---|---|---|---|---|
| 29 | $CH_2=CHCH_2$ | $C_6H_5CH=CHCO$ | $C_{20}H_{18}O_4$ | 224-226 | 3 | semisolid |
| 30 | $CH_2=CHCH_2$ | $p\text{-}CH_3OC_6H_4CO$ | $C_{19}H_{18}O_5$ | - | - | mp 178° |
| 31 | $CH_2=CHCH_2$ | $C_6H_5CH_2CH_2CO$ | $C_{20}H_{20}O_4$ | 227-235 | 7 | 1.5561 |
| 32 | $CH_2=CHCH_2$ | $(CH_3)_2CH\text{-}CH(CH_2)CH_2CH_2C(CH_3)CO$ | $C_{21}H_{28}O_4$ | 151-161 | 1 | 1.5344 |
| 33 | $C_4H_9$ | $CH_3CO$ | $C_{14}H_{18}O_4$ | 93 | 0.03 | 1.5265 |
| 34 | $C_4H_9$ | $CH_3CH_2CO$ | $C_{15}H_{20}O_4$ | 127 | .08 | 1.5281 |
| 35 | $t\text{-}C_4H_9$ | HCO | $C_{13}H_{16}O_4$ | 153-160 | 12 | 1.5470 |
| 36 | $t\text{-}C_4H_9$ | $CH_3CO$ | $C_{14}H_{18}O_4$ | 146-156 | 5 | 1.5081 |
| 37 | $t\text{-}C_4H_9$ | $CH_3CH_2CO$ | $C_{15}H_{20}O_4$ | 140-145 | 2 | 1.5150 |
| 38 | $t\text{-}C_4H_9$ | $(CH_3)_2C=CHCO$ | $C_{17}H_{22}O_4$ | 145-160 | 3 | 1.5288 |
| 39 | $t\text{-}C_4H_9$ | $(CH_3)_3CCO$ | $C_{17}H_{24}O_4$ | 144-164 | 12 | 1.5475 |
| 40 | $t\text{-}C_4H_9$ | $C_6H_5CH_2CO$ | $C_{20}H_{22}O_4$ | 220-230 | 5 | 1.5557 |
| 41 | $CH_3C(=CH_2)\text{-}CH$ | $CH_3CO$ | $C_{14}H_{16}O_4$ | 107 | .05 | 1.5362 |
| 42 | $CH_3C(=CH_2)\text{-}CH$ | $CH_3CH_2CO$ | $C_{15}H_{18}O_4$ | 103 | .05 | 1.5328 |
| 43 | $C_5H_{11}$ | $CH_3CO$ | $C_{15}H_{20}O_4$ | 118 | .1 | 1.5328 |
| 44 | $C_5H_{11}$ | $CH_3CH_2CO$ | $C_{16}H_{22}O_4$ | 105 | .1 | 1.5390 |
| 45 | $(CH_3)_2(C_2H_5)C$ | $CH_3CO$ | $C_{15}H_{20}O_4$ | 168-182 | 13 | 1.5192 |

Table 1.--Continued

| Item No. | R | R' | Empirical formula | Boiling point | | $N_D^{25}$ |
|---|---|---|---|---|---|---|
| | | | | °C. | mm./Hg | |
| 46 | $\overline{CH_2(CH_2)_4CH}$ | $CH_3CO$ | $C_{18}H_{20}O_4$ | 130-140 | 0.3 | 1.5481 |
| 47 | $\overline{CH_2(CH_2)_4CH}$ | $CH_3CH_2CO$ | $C_{17}H_{22}O_4$ | 183-188 | 12 | 1.5600 |
| 48 | $\overline{CH_2(CH_2)_4CH}$ | $(CH_3)_2C=CHCO$ | $C_{19}H_{24}O_4$ | 161-175 | 6 | 1.5660 |
| 49 | $\overline{CH_2(CH_2)_4CH}$ | $C_6H_5CO$ | $C_{21}H_{22}O_4$ | 183-193 | 12 | 1.5760 |
| 50 | $C_6H_5$ | $CH_3CO$ | $C_{16}H_{14}O_4$ | 177 | 2 | 1.5770 |
| 51 | $C_6H_5CH_2$ | $CH_3CO$ | $C_{17}H_{16}O_4$ | 207-215 | 3 | 1.5700 |
| 52 | $C_6H_5CH_2CH_2$ | $C_6H_5CH_2CO$ | $C_{24}H_{22}O_4$ | - | - | *1.5707 |
| 53 | $C_6H_5CH_2CH_2CH_2$ | HCO | $C_{18}H_{18}O_4$ | 171 | .05 | 1.5905 |
| 54 | $C_6H_5CH_2CH_2CH_2$ | $CH_3CO$ | $C_{19}H_{20}O_4$ | 183 | .8 | 1.5678 |
| 55 | $C_6H_5CH_2CH_2CH_2$ | $(CH_3)_2C=CHCO$ | $C_{22}H_{24}O_4$ | 191-210 | 3 | 1.5570 |
| 56 | $C_6H_5CH_2CH_2CH_2$ | $C_6H_5CH_2CO$ | $C_{25}H_{24}O_4$ | - | - | *1.5754 |

* Indicates product is liquid which could not be distilled without decomposition.

Table 2.--Screening tests of esters of piperonyl alcohols

| Item No.1/ | Ent No. 2/ | Mosquito larvicide | Louse toxicant | Chigger toxicant | Mosquito repellent | Synergist body louse | Synergist house fly |
|---|---|---|---|---|---|---|---|
| 1 | 20415 | 1 | 2 | 3 | 3 | - | inef. |
| 2 | 20433 | 2 | 4A | 4 | 1 | 3 | - |
| 3 | 20431 | 1 | 1 | 4 | 1 | 3 | - |
| 4 | 20460 | 2 | 1 | 1 | 1 | - | - |
| 5 | 20514 | 1 | 1 | 1 | 1 | 1 | inef. |
| 6 | 20719 | 2 | 1 | 1 | 1 | - | - |
| 7 | 20434 | 2 | 1 | 1 | 1 | inef. | - |
| 8 | 20437 | 1 | 1 | 1 | 1 | inef. | - |
| 9 | 20093 | 2 | 1 | 4 | 1 | inef. | inef. |
| 10 | 20720 | 2 | 1 | 2 | - | - | - |
| 11 | 20718 | 4 | 1 | - | 1 | - | - |
| 12 | 20275 | 1 | 1 | - | 1 | - | - |
| 13 | 20089 | 1 | 1 | 4 | 1 | 4 | inef. |
| 14 | 20090 | 1 | 1 | 4 | 1 | 4 | inef. |
| 15 | 20529 | 1 | 1 | 4 | 1 | - | - |
| 16 | 20339 | 4 | 1 | 4 | 1 | 3 | inef. |
| 17 | 20616 | 2 | 3 | 3 | 1 | - | 3 |
| 18 | 5004 | 2 | 1 | - | 1 | 3 | - |
| 19 | 20083 | 1 | 1 | 4 | 1 | 4 | inef. |
| 20 | 20357 | 3 | 2 | 3 | 1 | 3 | 3 |
| 21 | 20135 | 3 | 3 | 3 | 1 | 4 | 4 |
| 22 | 20139 | 2 | 1 | 1 | 1 | inef. | inef. |
| 23 | 20359 | 2 | 1 | 1 | 1 | - | - |
| 24 | 20142 | 2 | 1 | - | 1 | 4 | - |
| 25 | 20137 | 2 | 2 | 1 | 1 | inef. | inef. |
| 26 | 20721 | 2 | 1 | 2 | 1 | - | - |
| 27 | 20084 | 2 | 2 | 1 | 1 | - | - |
| 28 | 20136 | 3 | 2 | 3 | 1 | 3 | 3 |
| 29 | 20134 | 2 | 1 | 1 | 1 | inef. | 3 |
| 30 | 20111 | 1 | 1 | 1 | - | - | - |
| 31 | 20515 | 1 | 1 | 1 | 1 | - | 4 |
| 32 | 20332 | 1 | 3 | 3 | 1 | 4 | inef. |
| 33 | 20391 | 2 | 4 | - | 1 | - | - |
| 34 | 20392 | 3 | 4 | 4 | 1 | - | - |
| 35 | 20464 | 1 | 3 | 3 | 2 | - | - |
| 36 | 20463 | 1 | 4 | 4 | 2 | - | - |
| 37 | 20358 | 2 | 2 | 4 | 1 | - | - |
| 38 | 20482 | 3 | 1 | 2 | 2 | 3 | inef. |
| 39 | 20485 | 1 | 1 | 4 | 2 | 3 | inef. |
| 40 | 20516 | 3 | 1 | 1 | 1 | 3 | inef. |
| 41 | 20395 | 1 | 1 | 4 | 1 | - | - |
| 42 | 20396 | 1 | 1 | 2 | 1 | - | - |
| 43 | 20393 | 3 | 4A | 4 | 1 | - | - |
| 44 | 20394 | 3 | 4 | 4 | 1 | - | inef. |
| 45 | 20736 | 1 | 1 | 4 | 1 | 4 | inef. |
| 46 | 20417 | 2 | 4 | 4 | 1 | - | inef. |

Table 2.--Continued

| Item No. 1/ | Ent No. 2/ | Mosquito larvicide | Louse toxicant | Chigger toxicant | Mosquito repellent | Synergist body lice | Synergist house fly |
|---|---|---|---|---|---|---|---|
| 47 | 20461 | 3 | 4A | - | 1 | - | inef. |
| 48 | 20483 | 3 | 4A | 4 | 1 | 3 | 3 |
| 49 | 20462 | 3 | 4A | 4 | 1 | - | - |
| 50 | 20247 | 1 | 1 | 2 | 1 | - | - |
| 51 | 20561 | 2 | 1 | 2 | 1 | 3 | 3 |
| 52 | 20615 | 2 | 1 | 1 | 1 | - | inef. |
| 53 | 20465 | 4 | 4 | 1 | 1 | - | - |
| 54 | 20436 | 3 | 1 | 1 | 1 | 4 | - |
| 55 | 20484 | 4 | 1 | 1 | 1 | 4 | 3 |
| 56 | 20614 | 2 | 1 | 1 | 1 | - | 3 |

1/ See table 1.

2 Identifying numbers for the Entomology Research Branch compounds.